X-RAY SPECTRA, ELECTRON STRUCTURE, AND PROPERTIES OF METALLIC COMPOUNDS OF TITANIUM

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X-RAY SPECTRA, ELECTRON STRUCTURE, AND PROPERTIES OF METALLIC COMPOUNDS OF TITANIUM

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ABSTRACT. This article presents the results derived from studying the X-ray spectra of the emission (secondary excitation method) and absorption of titanium in metal-like compounds of $TiH_{1.83}$ TiB_2, TiC, TiN and TiO. The multi-band structure of the energy spectrum, which is apparent in a wide energy interval of 25-30 eV encompassing the 2s-,2p-valent states of the metalloid and the Bd-, 4sp-state of titanium, closely coincides with the results derived from present-day theoretical calculations (Ref. 24).

At present, there are two fundamental concepts regarding the nature of the /680* interatomic bonds and the electron structure in metal-like compounds of transition metals with light elements (H, B, C, N, O). According to the first viewpoint (Ref. 1-3), the introductory phases must be regarded as metallic solid solutions of metalloid atoms with a considerable collectivization of their outer electrons and with the formation of a general conductivity band. If the energies of the outer 2p-states of the metalloid atoms are high as compared with the Fermi energy for metals, then electrons of the atoms B,C,N make a significant contribution to populating primarily the metallic d-band -- in the opinion of the authors (Ref. 1, 3-5). One of the arguments in favor of this hypothesis is the wide region of metalloid concentration, within which the compounds remain stable. This is a characteristic feature of metallic alloys. All of these compounds have good electroconductivity; many of them are superconductors.

Other authors (Ref. 6-11) propound the opposite hypothesis. They assume that 2p-valent electrons of metalloid atoms make a great contribution to forming the strong, directional metal-metalloid (Me-X) bonds, which is indicated by the great rigidity and brittleness of these compounds. The small change in the distance between the closest titanium atoms in several substances Ti, TiB_2, TiC, TiN and TiO (Table I) provides a basis for assuming that the observed variation in hardness and melting temperature is determined by the Me-X interaction, /681 rather than the Me-Me interaction (Ref. 12). This concept has served as the basis for theoretical calculations of the zonal structure and curve for the density state in TiC and TiN (Ref. 8). The dispersion curves E(k) for TiO have been calculated in (Ref. 13).

A large series of experimental studies was recently published (Ref. 5, 12, 14-18). These studies presented the results of investigating the electric resistance, the Hall effect, the paramagnetic susceptibility, the critical temperature of the superconducting transition, and the electron specific heat. The fundamental conclusion which may be reached on the basis of these studies is that

*Note: Numbers in the margin indicate pagination in original foreign text.

TABLE I

Compound	Microhardness (Diamond 7000)	Melting Temperature Degrees C	Distance Between The Closest Ti-Ti Atoms, Å
Ti	157 - 209	1725 - 1800	2.960
TiB_2	--------	2790	3.03
TiC	3200 - 3800	3140 - 3170	3.058
TiN	1500 - 2160	2950	2.992
TiO	1000 - 1300	1750	2.956
$TiH_{1.83}$	--------	--------	3.12

the different properties change with a change in the electron concentrations in the face-centered cubic carbides, nitrides, and their solid solutions, so that they may be interpreted in terms of the so-called model of "a rigid band". However, there are not enough data to form an opinion regarding the zonal structure of the energy bands, the nature of their population, and the interatomic interactions in these compounds.

This article reports upon and interprets the results derived from investigating the spectra of the emission (secondary excitation method) and absorption of titanium in the metal compounds TiB_2, TiC, TiN, TiO and $TiH_{1.83}$. Some of the X-ray spectral characteristics of these compounds were studied in (Ref. 19-22). In several cases, the research results are contradictory. After the study of Ern and Switendick was published (Ref. 24), it became apparent that it was necessary to perform a detailed analysis of the different X-ray spectral characteristics of these titanium compounds and to compare them with other physical properties (Ref. 5, 12, 14, 15, 18, 23). The study of Ern and Switendick contained a careful and reliable theoretical calculation of the structure of the electron-energy spectrum in TiC, TiN and TiO.

Method and Research Results

A description of the apparatus and the research method is given in (Ref. 29). The effective thickness of the absorbent for different compounds corresponded to the 6-micron thickness of metallic titanium. The maxima of the $K^{II}_{\beta 5}$-band for different titanium compounds was chosen in accordance with data given in (Ref. 19). The intersection point of the emission and absorption curves approximately characterizes the position of the Fermi level in the energy scale. The spectra thus compiled for the emission and absorption are shown in Figure 1. The energy of the intersection point for the curves of the β_5-band and the K-edge of the metallic titanium absorption was chosen as the zero reading.

For purposes of clarity and to make it easier to interpret the spectra obtained, the region of the initial (long wave) absorption was separated from the

basic edge by drawing a dashed line 1, which smoothly joined the absorption curve going upwards after a sharp bend (or minimum) designated by the letter m. A similar separational procedure is employed for the emission spectra.[1]

The absorption bands thus delineated are bounded on the shortwave side by the dashed line 2, and are designated by K_{II} (for TiC it essentially consists of two parts: K_I and K_{II}). In the emission spectra, the bands are bounded /682
by the dotted line 3, and are designated by $K^I_{\beta 5}$. There is practically no $K^I_{\beta 5}$-band in TiC.

Figure 1 shows that the investigated metallic compounds of titanium may be characterized by a clearly-expressed multiband structure of the electron-energy spectrum, which amounts to 25-30 eV.

Discussion of the Results /683

a) Form and Position of the Energy Bands

In order to reliably interpret the observed patterns in the change of the X-ray spectra, it is advantageous to discuss them concurrently with the data given in the study by Ern and Switendick (Ref. 24). The structure of the energy bands may be calculated by the method of connected plane waves for the energy region, which encompasses the metalloid 2s- and 2p- and titanium 3d- and 4s-states. In order to obtain reliable curves for the state density, the authors (Ref. 24) calculated the value of E(k) for 256 points uniformly distributed in the Brillouin zone.

Figure 2 presents curves for the state density for three titanium compounds, compiled with a step interval of $\Delta E = 1{,}02$ eV (Ref. 24). The energies of the Fermi levels were obtained by arranging 8 (TiC), 9 (TiN) and 10 (TiO) outer electrons by energy states, beginning with the lowest 2s-band. According to (Ref. 24), the lowest-energy band has primarily a 2s-like nature (it is not shown in Figure 2 for TiO). In X-ray spectra, it appears in the form of the $K_{\beta''}$-band (Figure 1) (Ref. 26). The band which follows in terms of energy is formed as a result of the hybridization of 2p metalloid and 3d titanium electron states. According to (Ref. 5, 24), this band is the basic valence-connecting band arising as a result of the strong interaction between the metal-metalloid (Me-X) closest atoms, located in the octahedral positions of a NaCl-type lattice. According to our data and the data given in (Ref. 27, 19, 22, 25), the electron transitions from this hybridized connecting (2p + 3d)4p-band leads to the /684
formation of the most intense X-ray $K^{II}_{\beta 5}$-band (Figure 1). Its great intensity is related to the large admixture of p-states.

[1] The method presented here for separating the spectra is approximative and arbitrary. Nevertheless, this procedure is frequently employed in spectroscopy and is justified.

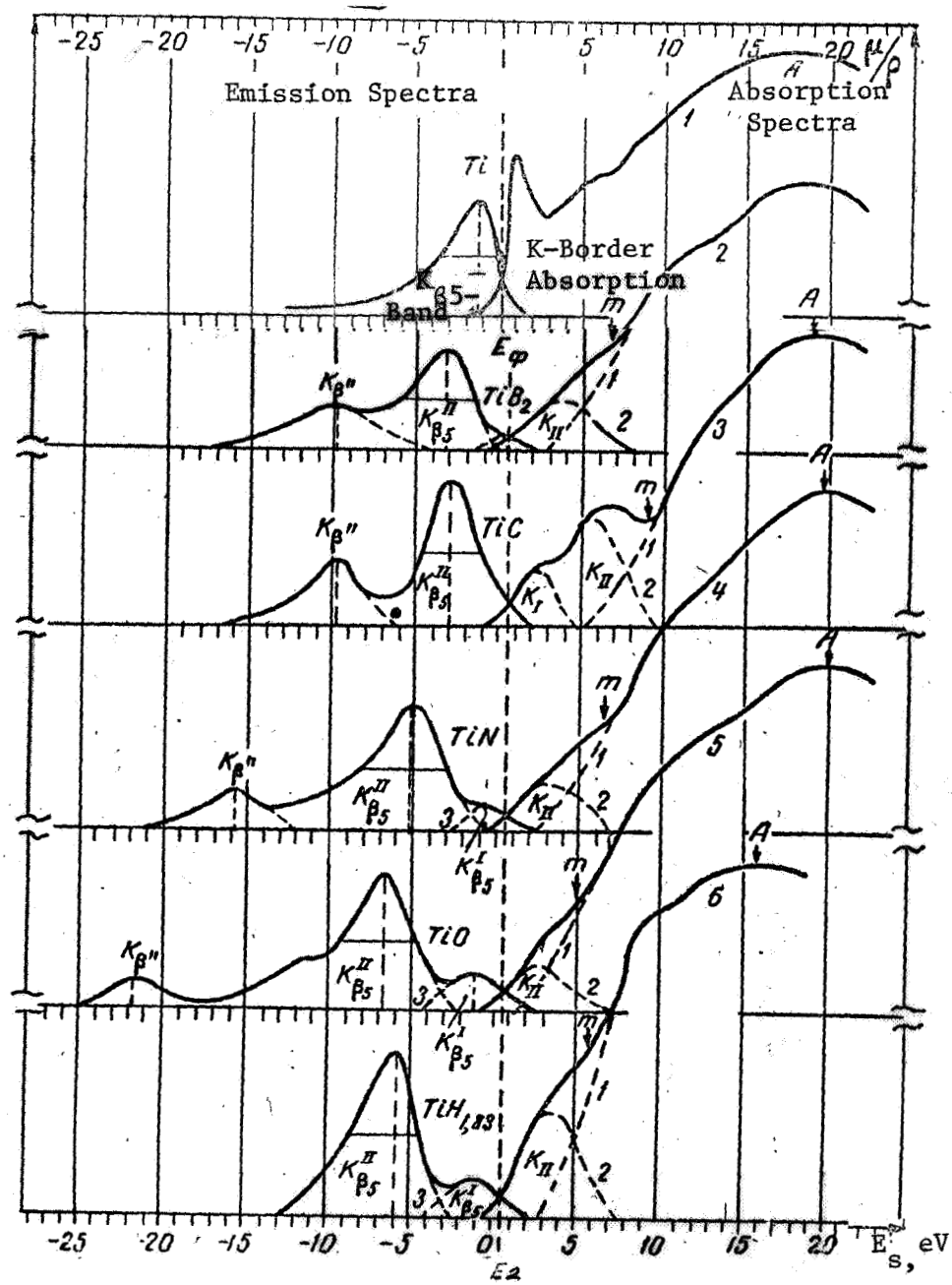

Figure 1. The K-Spectra of the Emission and Absorption of Titanium in Metal Compounds With Light Elements.

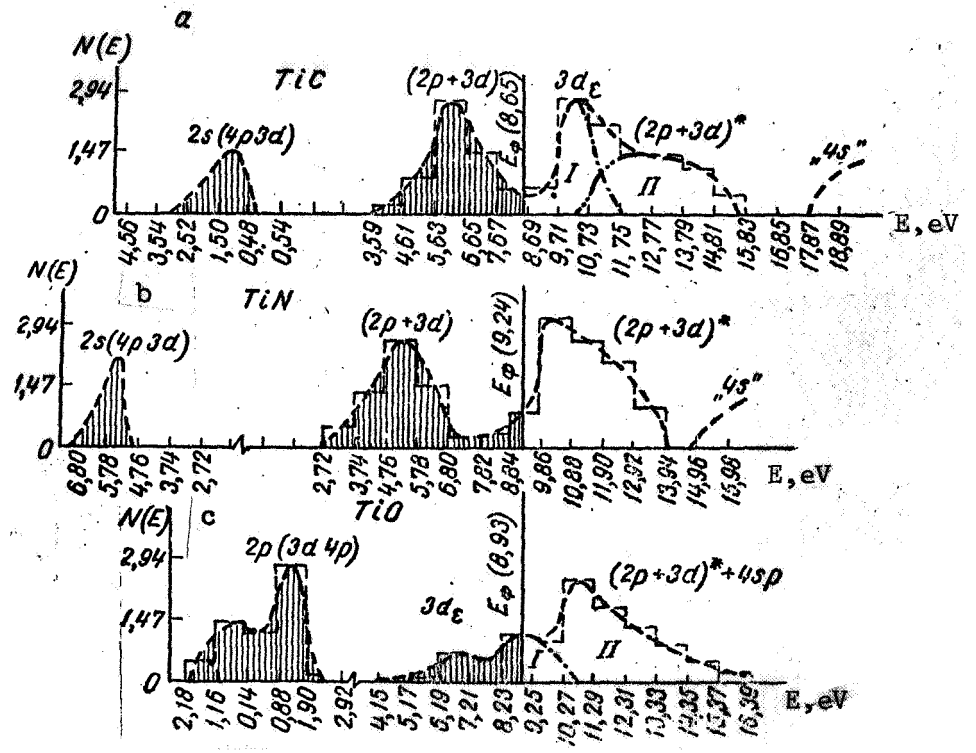

Figure 2. Curves for the Density of Electron States For Energy Bands in TiC, TiN, and TiO (Ref. 24).

TABLE II. CHARACTERISTICS OF THE X RAY EMISSION BANDS AND THEIR COMPARISON WITH DATA FROM THEORETICAL CALCULATIONS (REF. 24)

Compound	$(K^{II}_{\beta_5} - K_{\beta''})$ max eV			$(E_{2p+3d} - E_{2s})$max [24] eV	Asymmetry Index of the Band $K^{II}_{\beta_5}$		
	H.K.*	[19]	[22]		H.K.*	[19]	[24]**
TiB_2	6,6	—	—	—	1,72	1,67	—
TiC	7,0	7,0	7,0	7,1	0,80	0,81	0,7
TiN	10,7	10,0	11,0	10,7	1,31	1,32	1,20
TiO	15,0	15,2	15,5	15,1	1,33	1,32	1,36
$TiH_{1,83}$	—	—	—	—	2,0	—	—
Ti	—	—	—	—	2,1	2,03	—

* Data from the present article.

** Asymmetry index of the curve for the state density for (2p+3d)-valent band (according to the authors calculation).

Table II presents the distances (in electron volts) between the intensity maxima of $K^{II}_{\beta 5}$- and $K_{\beta''}$-bands for the investigated titanium compounds, which are compared with the energy difference in the maxima of the state densities for the

(2p+3d)- and 2s-energy bands (Ref. 24). It is apparent that there is very good agreement between the experimental and theoretical data. A comparison of Figures 1 and 2 show that there is good agreement in terms of the form of the investigated bands. Table II presents a comparison of the experimental values of the asymmetry index of $K^{II}_{\beta 5}$-bands with the values which we calculated based on the curves for the state density for TiC, TiN and TiO (Figure 2). These data agree very well. There is an apparent forking of the 2p(3d4s)-band on the curve for the TiO state density. A similar phenomenon is observed on the experimental curve of the $K^{II}_{\beta 5}$-band.

On each of the curves in Figure 2, above the Fermi level there is a single conductivity band, which is separated from the valence band by a deep minimum of the state density (TiC and TiN), or by the intermediate band (TiO). In accordance with (Ref. 24), we shall call them anti-connecting (2p+3d)*-bands. In the case of TiN and TiO, the form of these bands (Figure 2) is similar to the experimentally observed K_{II}-bands of absorption (Figure 1, Curves 5 and 4). We shall investigate below the reason for the lack of agreement between the theoretical curve and the experimental curve for TiC.

In Figure 2a-b, there is either a break, or a sharp drop in the state density (deep minimum), between the anti-connecting (2p+3d)*-band and the band which has arbitrarily been called the 4s-band by Ern. The width of this "forbidden zone" greatly decreases during the transition from TiC to TiN, and it practically changes into a wide and smooth minimum of the state density in TiO (Figure 2). A similar picture is observed on the curves of the absorption spectra (Figure 1). For TiC, there is a sharply expressed minimum m above the initial absorption region K_I. The depth of this minimum must greatly increase after the spectrum has been adjusted over the width of the inner level (Ref. 28). In the absorption spectra of TiN, this minimum is expressed more faintly, and /685 for TiO it changes into a wide, smooth bend. According to (Ref. 24), the reason for the formation of this break (minimum) may be found in the fact that the Γ_1-Γ_1 (2s-4s) interaction forces out the 4s-like titanium band in the direction of higher energies above the series of the 3d-bands. With an increase in the nucleus charge of the metalloid atom, the 2s-band becomes more localized, due to which the 4s-band is forced out to a lesser extent, and its energy is decreased. For TiO, the upper portion of the (3d+2p)*-band becomes strongly hybridized with the 4s-states.[2]

The formation of a clearly expressed minimum or a bend in the region m (Figure 1) now becomes physically understandable, and represents an argument for the validity of separating the band of K_{II} from the absorption cotinuum. Consequently, in this energy region, the theory indicates the correct approach for interpreting the composite structure of X-ray spectra, which is characteristic

[2]The sharp rise in the absorption curve, observed above the minimum m indicates that in actuality, not a 4s-like band is formed in this energy region, but rather a 4sp-hybridized band. The 4p-states of titanium were not taken into account in explicit form in the calculations of Ern.

for many similar compounds of transition metals.

b) Origin of the Bands and Energy Distribution of the States

In the case of K-spectra, the intensity of X-ray bands, produced by transitions from the 4s- and 3d-electron states, will be primarily determined by the admixture of p-states-- i.e., by sp- or dp-hybridization. This is of great importance in determining the nature of the interatomic interactions (chemical bonds).

Figure 3 presents a graphic comparison of these characteristics with the spectra. The energy (calculated at 32 highly symmetrical points in the Brillouin zone) distribution of the states having different symmetry, (2s, 2p, 3d, 4s, and 4p) is shown graphically under each spectrum (Ref. 24).[3]

The height of the vertical line for each state shows the charge content (in percents) in the sphere of titanium or the metalloid. The notation for the different states is given below on the right. In all of the curves and graphs, the origin starts from the Fermi level. It may be seen from the figure that a low-energy band actually primarily consists of 2s-states of the metalloid, and that it occurs in the titanium spectra to the extent that there is an admixture of 4p-states in it (we must emphasize that it is 4p-, and not 2p-states: the admixture of the former amounts to 4-10%, whereas the admixture of the latter does not exceed hundreds or tenths of a fraction of a percent). The following problem may then be formulated: do we employ the term "crossover transitions" for the given band (Ref. 26). We might add that neither in the K-spectra of nitrogen (TiN), nor in the K-spectra of carbon (NbC, TaC) (Ref. 31), on the long wave side, are there any indications of the occurrence of a band caused by direct 2s(pd)-transitions, in contrast to the so-called "crossover transitions" leading to the formation of the $K_{\beta''}$-band of the compound metallic component.

The spectra and graphs also show that the 2s-like band (with a small admixture of 4p3d-states) in several compounds TiC, TiN and TiO continuously contracts, and its intensity with respect to the intensity of the $K^{II}_{\beta 5}$-band greatly decreases (Table III). Localization of the 2s-states is confirmed by the great reduction in the energy of the $K_{\beta''}$-band with respect to the Fermi level. /687

The graphs show that the 2p-state of the metalloid and the 3d-(with an admixture of 4p-) state of titanium make the basic contribution to the formation of the valent, strongly connecting $K^{II}_{\beta 5}$-band. The contribution of the 4p-states is very small, and there are practically no 2s-states. The conclusion may thus be reached that only 2p-electrons participate in the Me-X bonds from the side of the metalloid atoms, and only 3d-electrons participate from the side of the titanium atoms and, to a lesser extent, the 4p-state. In accordance with the three-dimensional symmetry of the octahedron, out of five of the 3d-orbitals only doubly degenerated d_{γ}-orbitals can be included in the hybridization with

[3]We (the authors) made a recalculation of the energy with respect to the Fermi level and a graphic representation of the states having different symmetry. A similar recalculation for TiO and a comparison with the spectra was made in (Ref. 30) (Table I), which was published when this article was being written.

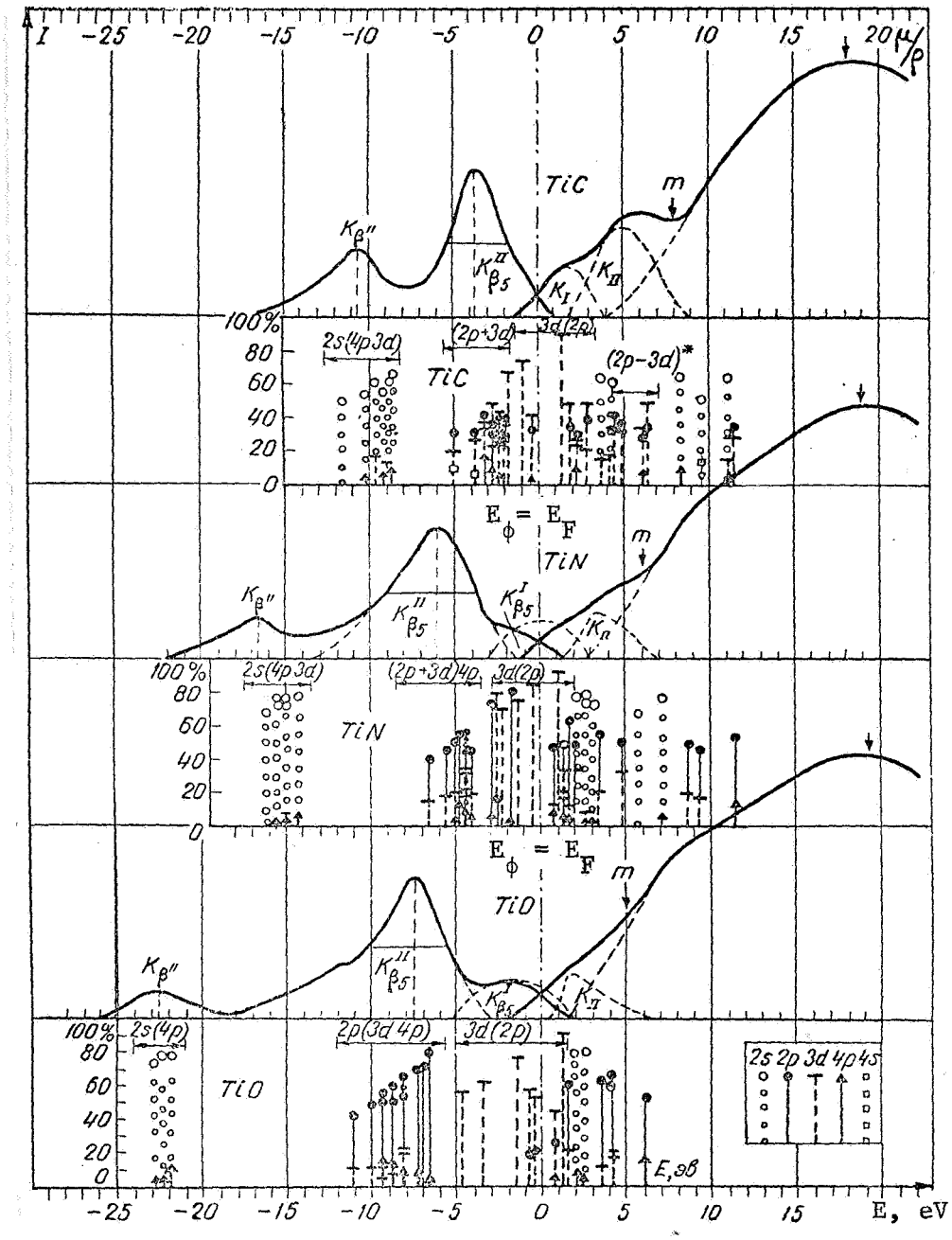

Figure 3. Energy Distribution of the Charge Density For States Having Different Symmetry (2s, 2p, 3s, 4s and 4p) (Ref. 24), and the Structure of the X-Ray Bands of Emission and of Absorption.

2p- and 4p-states -- in other words, the e_g-states, whose wave function symmetry is very suitable for this hybridization (Ref. 5).[4]

TABLE III. RELATIVE INTENSITIES AND POSITION OF THE MAXIMA OF THE EMISSION BANDS (WITH RESPECT TO THE FERMI LEVEL) AND THEIR COMPARISON WITH DATA FROM THEORETICAL CALCULATIONS (REF. 24) (ESTIMATES OF THE CORRESPONDING VALUES ARE GIVEN BY THE AUTHORS OF THIS ARTICLE)

Compound	$\left(\frac{IK_{\beta''}}{IK^{II}_{\beta_5}}\right)_m$ H.K.*	$\left(\frac{N(E)_{2s}}{N(E)_{2p+3d}}\right)_m$ [24]	$\left(\frac{IK^{II}_{\beta_5}}{IK_{\beta_1}}\right)_m$ [19]	$N(E)^m_{2p+3d}$ [24]	Position $K^{II}_{\beta_5}$ Band eV		$K_{\beta''}$ Band eV	
					H.K.*	[24]	H.K.*	[24]
Ti	—	—	0,31 (0,0157)**	—	—	—	—	—
TiB_2	0,42	—	0,32	—	—	—	—	—
TiC	0,46	0,56	0,45	2,70	—3,6	—2,5	—10,5	—9,7
TiN	0,32	0,81	0,41	2,51	—5,9	—3,9	—16,5	—14,6
TiO	0,19	0,80	0,43 (0,0225)*	2,76	—7,5	—7,7	—22,5	—22,4
$TiN_{1,83}$	0,0	—	—	—	—	—	—	—

* Data from the present study.
** Ratio of the integral intensities (Ref. 22).

For TiC in the region of the (2p+3d)-connecting band, the ratio of the charge density distributed in the 2p-states approximately equals the charge density distributed over the 3d4s-states. This means that the Me-X bonds in TiC are primarily covalent. In the transition to TiN, and in addition to TiO, the charge density, distributed in the sphere of nitrogen and then in the oxygen sphere, subsequently increases substantially. For TiO, the contribution of the 2p-states to the valent band greatly exceeds the contribution of the 3d4ps-states. It thus follows that in the series TiC-TiN-TiO, the degree of the bond covalence decreases due to an increase in the ion component of the chemical bond. This may apparently explain the significant decrease in the melting temperature and the microhardness in this series of compounds (Table I).

It may be shown that the number of electrons populating the connecting band in each compound barely changes, and equals 6 electrons per elementary unit (since for TiC and TiN the area under each curve for the state density of the 2s-band corresponds to two electrons). In this sense, it may be assumed that the bond between the metal-metalloid atoms is saturated. In the transition from metallic titanium to the compounds, the intensity in the maxima of $K^{II}_{\beta 5}$ (for TiO it is an integral) increases by almost a factor of one and one half, which corresponds to an increase in the number of electrons in the band from 4 to 6.

[4] The valence-active p^3-state of the metalloid and the $d^2_\gamma p$-state of the metal are characterized by greatly extended clusters of the charge density, directed toward the closest octahedrally-distributed neighbors, which leads to strong overlapping of their wave functions.

It may be seen from Figures 1 and 2 that the energies of the Fermi levels /688
for all three compounds remain practically unchanged (stable), in spite of the fact that the electron concentration changes from 8 for TiC up to 10 for TiO. At the same time, the energy of the maximum of the $K^{II}_{\beta 5}$-band decreases from minus 3.6 (TiC) to minus 7.5 eV (TiO) (Table III) with the simultaneous formation (TiN) and the almost complete formulation (TiO) of a new $K^{I}_{\beta 5}$-band, located on the shortwave side of $K^{II}_{\beta 5}$. There are weak indications of this band in the emission spectra of TiC. Figure 3 shows that the excess electron concentration, which increases in the series of compounds TiC, TiN and TiO, goes into the successive population of this new energy band. A similar picture is observed on the curves of the state density. Many authors are of the opinion (Ref. 8, 27, 25, 5) that this band is basically caused by the metal-metal (Me-Me) interaction, which is strong in these compounds (Ref. 24), since the distance between the closest Ti-Ti atoms almost coincides with the distance in pure titanium (Table I). In accordance with the symmetry of the lattice of these compounds, the directions of the shortest distances for the Ti-Ti atoms are located between the coordinate axes in each plane of the cube xy, yz, zx. The d_{xy}-, d_{yz}-, and d_{zx}-states are suitable orbitals for these bonds. The wave functions of these states produce the maximum overlapping in these directions. Therefore, it is appropriate to call the (Me-Me)-band the d-or t_{2g} band.

From a concurrent examination of Figures 2 and 3, it may be readily seen that in the case of TiC there are in fact two bands[5] above the Fermi level, which we have designated by the numbers I and II. The fact that they are different in nature may be seen from the great lack of agreement in their relative heights; in Figure 2a, the sub-band I has a state density (at the maximum) which is approximately two times greater than the sub-band II, whereas the opposite is true in the absorption spectra (Figure 3) -- i.e., $(K_I/K_{II})_m=0.6$. This lack of agreement is caused by the influence of the quanta selection rules, which indicate in this case that the sub-band II (Figure 2) or K_{II} (Figure 3) contains a considerable admixture of p-states and is apparently an anti-connecting (2p+3d4p)*-band. The spectra together with the graphs[6] (Figure 3) definitely show that in TiC the 3d (2p)-band is not populated to a significant extend, and clearly appears in the absorption spectra in the form of the K_I-band.

The Fermi boundary must pass through the junction of the two slightly overlapping bands: (Me-X)-connecting band and the (Me-Me)-band, i.e., in the region of low state density values. According to the calculations of Ern (Ref. 24),

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[5] We made a tentative separation of the non-populated band, calculated by Ern for TiC, into two sub-bands: I and II. The separation of the d_ε-band becomes even more significant in the case of TiO (Figure 2c).

[6] The parentheses indicate the states which represent an admixture to the fundamental states. This notation pertains to other bands, in addition to the connecting (2p + 3d)-band.

for TiC there are $N(E)_F$ = 0.38 electron states per molecule, which is substantiated by data on the electron specific heat ($N(E)_F$ = 0.23) and the magnetic susceptibility (~ 0.49) (Ref. 5). In TiN, the Fermi boundary passes somewhere through the middle section of the 3d(2p4p)-band, dividing it into two, approximately equal halves. In the spectra, this takes the form of a $K^I_{\beta 5}$-band of emission, and the remaining half -- in the form of a K_I-band of absorption. If both of these halves, which are divided by the Fermi level, are arbitrarily joined in the form of a dotted curve, we may obtain a rough idea of the width of this band. Finally, for TiO the electron concentration amounts to approximately 10 electrons per primitive cell, which leads to considerable population of the 3d-like band. Its width at half-height amounts to approximately 5 eV, and 7 eV along the base. According to a theoretical calculation (Ref. 13), the width of the 3d-band is 6 eV in TiO. /689

Based on the X-ray spectra, the capacity of the d_ε-band is about 3 electrons per primitive cell. Figures 2c and 3 show that the d_ε-band in TiO is not completely populated by electrons. Incidentally, we should note that in the transition from TiC to TiO in this energy band the admixture of 2p-states becomes smaller. This is apparently due to an increase in the ion component of the chemical bond, which leads to a greater separation of the bands which are genetically different.

A study is made in (Ref. 32) of the L_{III}-band of emission (p-ds-transitions) of titanium in the compounds TiB_2, TiC, TiN, TiO. The authors (Ref. 32) showed that for TiC the emission L_{III}-band is displaced toward smaller energies, and for TiN and TiO toward greater energies, as compared with pure titanium. The authors thus reached the conclusion that nitrogen and oxygen are electron acceptors, whereas carbon is a donor. It is possible that this conclusion is correct, but not unequivocal. For TiC, the d_ε-band is located above the Fermi level (Figure 3). Therefore, the electron transitions are essentially accomplished from one strongly hybridized 2p3d-band, whose state density maximum (See Figures 2 and 1) is shifted toward smaller energies with respect to the $K_{\beta 5}$-band of pure titanium.

The situation is different in the case of TiN, and particularly TiO, in which the d_ε-band is almost 1/2 or 2/3 populated. On the one hand, in these compounds there is an increase in the population of the d-band, which is immediately adjacent to the Fermi boundary. On the other hand, the (Me-X)-band becomes more like a 2p-band. Therefore, the probability of radiative transitions from the d-band considerably exceeds the probability of transitions from the 2p(3d4p)-band. As a result of this, the most intense portion of the emission L_{III}-band becomes more short-waved than the L_{III}-band of pure titanium.

It was shown in (Ref. 23) that in titanium dihydride the Fermi boundary is located close to the minimum of the state density -- i.e., at the junction of two slightly intercepting bands. The X-ray spectra indicates this (Figure 1).

The structure of the energy bands in TiB_2 has much in common with the energy bands of TiC (Figure 1), in spite of the fact that the crystalline structure of the diboride is more complex . The widening of the $K_{\beta''}$-band and its approaching the fundamental connecting $K^{II}_{\beta 5}$-band is absolutely valid. Consequently, in TiB_2 the basic factor determining the main characteristics of the electron-energy spectrum is the presence of two essentially different types of interatomic interactions:[7] Ti-B and Ti-Ti (the distance between the titanium atoms equals 3.024 Å).

c) Electron Structure and Physical Properties

The information obtained on the zonal structure of the energy spectrum may be used as a basis for understanding and more reliably interpreting an entire series of physical (electron) properties of metal-like compounds (Ref. 3,5, 9-12, 14-18, 23, 33-36), and primarily the carbides, nitrides, and their solid solutions. Figure 4 presents the dependence of the critical temperature of the superconductive transition T_{cr} on the total number of valent-active electrons Σ belonging to the primitive cell in different compounds and their solid solutions with the NaCl structure. The notation is given above to the left. The values of T_{cr} are taken from (Ref. 33, 34, 14) and other sources in the literature. According to the empirical rule of Mattinias (Ref. 35), T_{cr} depends on the average number of valent electrons per atom, which is shown in Figure 4. Pines (Ref. 36) assumed an approximate relationship between T_{cr} and the state density at the Fermi boundary N(E):

$$T_{cr} = \Theta_D \exp\left[-\frac{1}{N(E)V}\right],$$

where Θ_D is the Debye temperature and V is the interaction parameter. It was shown in (Ref. 37) that the interaction parameter V is roughly constant, and equals 0.4 eV for a large group of alloys or compounds of transition metals.

The conclusion may be drawn from the statements given above and Figure 4 that the dependence of the critical temperature on the electron concentration in compounds with a face-centered cubic lattice approximately reflects the behavior of the density curves for electron states of the d_ε-band (for I, II and III periods), modified by the interaction parameter V and the Debye temperature. It also follows from Figure 4 that part of the d_ε-band may contain about three electrons per atom, and that the state density maximum corresponds to approximately 9.7 electrons per primitive cell.

Further corroboration of the simple zonal structure close to the Fermi

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[7] Taking into account the interaction between boron atoms which produce two-dimensional lattices in the crystal, if the interaction appears in the K-spectra of titanium, then it will only appear as widening of the $K_{\beta''}$-band.

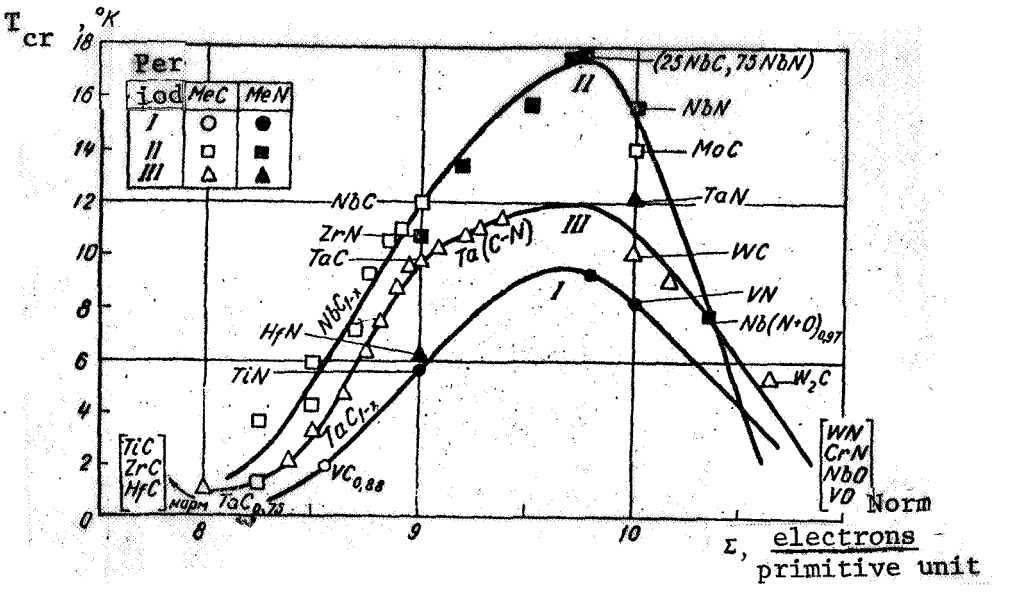

Figure 4. Dependence of the Critical Temperature of the Superconducting Transition on the Electron Concentration in Carbides and Nitrides of Transition Metals of I, II and III of Large Periods.

level in the introductory phases may be obtained from data on the magnetic susceptibility, the temperature dependence of the Hall effect, and other properties (Ref. 14-18). The isoelectron compounds -- for example, NbC, ZrN and TaC or TiC, ZrC and HfC -- and also solid solutions show considerable agreement in terms of electron properties. It is found that the form of energy bands in these compounds is not very sensitive to the replacement of atoms of one metal by atoms of another metal (within the limits of the IV, V, and even VI groups), or to the replacement of carbon atoms by nitrogen atoms -- only the concentration of the valence electrons changes. A simple explanation of these phenomena may be found in the fact that, when the electron concentration increases (beginning with 8), additional electrons in a series of compounds ZrC-NbC-NbN (in our case TiC-TiN-TiO) begin to populate a new energy band. This band is almost empty for ZrC (Ref. 14) or TiC (Figure 3) and, based on Figure 4, it is entirely populated for WN, NbO, CrN (Σ = 11). /691

Along with these general and fundamental characteristics of the electron-energy spectrum of the compounds under consideration, it is natural to expect individual characteristics caused by a differing degree of ionicity of the intra-atomic bonds, by the different nature of defects in the crystalline lattice, and by the differing extent to which the adjacent energy bands overlap.

It has already been pointed out above that the process by which the d-like band is populated in metal-like compounds begins with electon concentration which approximately equals 8 (ScN, YN, TiC, ZrC, HfC), and terminates for a total electron concentration which is close to 11 electrons per primitive cell (CrN, WN, VO, NbO). It may be readily seen that these two limiting concentrations

of valence electrons represent in essence the boundaries for the existence of stable metal-like compounds within whose limits electron concentration, and consequently the extent to which the b-sub-band is populated, may continuously change just as when transition metals are alloyed together (Ref. 38). This similarity has led many researchers (Ref 3-5, 14-16) to identify the electron structure of these compounds with the electron structure of the transition metals and alloys. This concept may be valid to a certain extent, because the electron properties which they studied are determined primarily by the structure of this (Me-Me)-band, the degree to which it is populated, and the state density at the Fermi boundary.

The basic valent-connecting band, which is apparent in the K-spectra in the form of a $K^{II}_{\beta 5}$-band, remains essentially concealed for the majority of electron properties (it is located below the Fermi level) and has no significant influence upon it. The origin of this band, its structure and energy position have, however, a decisive influence upon other properties (hardness, melting temperature, brittleness, etc), which are primarily caused by the ion subsystem. Those researchers who primarily directed their attention to this series of properties naturally defended another viewpoint. According to this viewpoint, the nature of metal-like compounds under consideration is primarily determined by the presence of strong metal-metalloid bonds (covalent or ion-covalent).

The results derived from this study, the data from theoretical calculations and an analysis of the different properties show that the two concepts investigated above regarding the nature of metal-like compounds comprise a single whole. They only reflect different sides of the complex electron structure of these compounds, and therefore there is no physical meaning in comparing them with each other.

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